

## Chemical conversion of woody biomass by supercritical water -Degradation of lignin-

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Chemical conversion of buna wood (*Fagus crenata* Blume) was made in supercritical water (>22.1MPa, >374°C). The treated wood was fractionated into the water-soluble portion, methanol-soluble portion, and methanol-insoluble residues. In this study, a characterization of the lignin was focused on the methanol-soluble portion and methanol-insoluble residue. The obtained methanol-soluble portion showed to be rich in lignin-derived products which had more phenolic hydroxyl groups than those in lignin of wood. The alkaline nitrobenzene oxidation analyses of the products in the methanol-soluble and methanol-insoluble portions exhibited a decrease of oxidation products under supercritical water treatment. Through a study with lignin model compounds,  $\beta$ -O-4 type lignin model compound was cleaved, whereas biphenyl type was not by supercritical water treatment. These observations clearly indicated that a preferential degradation of the ether linkages of lignin occurs in supercritical water.

### Introduction

The potential for the utilization of biomass as a source of useful chemicals and fuel has been a subject of renewed interest recently in response to depletion of the fossil resources. To be realized for utilization of biomass, various approaches to the conversion of biomass have been practiced such as pyrolysis, acid hydrolysis, and enzymatic hydrolysis. Besides these approaches, supercritical fluid has received increasing attention in a conversion of biomass resources. Saka et al. reported that main components of wood such as carbohydrates (cellulose and hemicelluloses) and lignin were separated to water-soluble and methanol-soluble portions after the supercritical water treatment, respectively.[1, 2] The water-soluble portion, which mainly consisted of glucose, xylose, and its derivatives, may have a potential for a source of ethanol fermentation. However, methanol-soluble portion, which mainly consisted of lignin-derived products, must be known in detail to be evaluated for its potential for utilization. This paper, therefore, presents information on the characteristics of methanol-soluble portion and methanol-insoluble residue derived from buna wood in order to provide a clue as to its utilization and to elucidate the mechanism of lignin degradation.

### Materials and methods

The supercritical water biomass conversion system used in this study was revised to be a batch-type reaction vessel [1]. Five ml of water was fed with 150 mg of buna (*Fagus crenata* Blume) flour to this reaction vessel, and then it was quickly heated by immersing it in the tin bath preheated at 500 °C. For lignin model compounds, 1 ml of water was used with 2 mg compound instead. To stop the reaction, the reaction vessel was immersed in the water bath to quench. After the supercritical water treatment, water-soluble portion was retrieved by filtration. The water-insoluble portions were washed with 10 ml of methanol for 10 minutes by sonication, and then separated to methanol-soluble portion and methanol-insoluble residue by filtration. Spectroscopic analyses and gel permeation chromatography (GPC) of the methanol soluble portion were carried out. Phenolic hydroxyl groups of the methanol-soluble portion and methanol-insoluble residue were determined by  $\text{FeCl}_3$  method and periodate oxidation method, respectively. Alkaline nitrobenzene oxidation analysis was also carried out. The model compound experiments using guaiacylglycerol- $\beta$ -guaiacyl ether and 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethyl-biphenyl were carried out. The model compounds (2 mg) were fed into the reaction vessel with 1 ml of water, and the supercritical treatments were carried out in the same manner as mentioned above. The resulting reaction mixtures were analyzed by using the high performance liquid chromatography (HPLC) which was equipped with the column (ODS-STRII C18).

### Results and discussion

The experimental conditions and the yields of fractionated portions were summarized in Table 1. Buna wood flour was almost completely solubilized in water and methanol by supercritical water treatment. In our previous experiment, it was clarified that water-soluble and methanol soluble-portions were mainly derived from carbohydrates and lignin, respectively.[2] Consequently, the following experiment was focused on the lignin-derived products in the methanol-soluble portion and methanol-insoluble residue.

Table 1 Experimental conditions and resulting fractions of wood as treated in subcritical water or supercritical water.

Treatment, time (s)	Condition		Yield (%)		
	Max temperature (°C)	Max pressure (MPa)	Water-soluble	Methanol-soluble	Methanol-insoluble
Subcritical, 10	330	50	51.2	10.5	38.3
Supercritical, 5	380	100	71.2	19.8	9.0
Supercritical, 8	400	115	73.7	17.8	8.5

Table 2 Determination of phenolic hydroxyl groups and nitrobenzene oxidation products in buna wood and fractionated wood as treated with subcritical or supercritical water.

Treatment, time	Content of Phenolic hydroxyl group (number / 100 of C <sub>6</sub> -C <sub>3</sub> )		Yield of nitrobenzene oxidation product (mol/ g of lignin)	
	Methanol-soluble	Methanol-insoluble	Methanol-soluble	Methanol-insoluble
Buna wood flour	-	14.1	-	2.1
Subcritical, 10	38.6	30.6	0.7	0.8
Supercritical, 5	42.0	14.1	0.5	0.2
Supercritical, 8	38.6	16.5	0.2	n.d.

The FT-IR and UV-VIS spectra of the methanol soluble portions showed the typical spectra of lignin. The absorbance at 280 nm in UV-VIS spectrum and that at 1600, 1510, 1425cm<sup>-1</sup> in FT-IR spectrum, which were assigned to aromatics, did not drastically change in three different treatment conditions. However, the absorbances at 350nm in UV-VIS spectrum and 1720 cm<sup>-1</sup> in FT-IR spectrum, which was assigned to carbonyl groups, increased with treatment temperature. As a results of GPC analyses, the molecular weight distribution of the methanol-soluble portion was ranged from 300 to 3000. These results suggested that lignin in buna wood is degraded and solubilized to methanol by supercritical water in keeping with aromatic nuclei.

Table 2 showed the results of phenolic hydroxyl group determination and alkaline nitrobenzene oxidation analyses. Phenolic hydroxyl group of lignin in buna wood was about 14 per 100 units of phenylpropane (C<sub>6</sub>-C<sub>3</sub>) residues, and that of methanol-soluble portion was about 40 units. Phenolic hydroxyl group of lignin in methanol-insoluble residue was also about 40 units per 100 of phenylpropane unit. The yields of the nitrobenzene oxidation products derived from lignin in methanol-soluble portion and methanol-insoluble residue were low, compared with those of buna wood. Phenolic hydroxyl group would, therefore, be produced by degradation of ether linkages of lignin, and low yields of nitrobenzene oxidation products implied that the lignin is rich in condensed-type linkages of lignin.

To simulate the reaction behaviors of lignin in supercritical water, model compound experiments using  $\beta$ -O-4 type and biphenyl type compounds were performed. As a results,  $\beta$ -O-4 type compound was cleaved into guaiacol and coniferyl alcohol by subcritical water treatment. Furthermore, in the case of supercritical water,  $\beta$ -O-4 type compound was completely disappeared and converted into guaiacol and some unidentified products. On the other hand, biphenyl type compound was very stable during its treatment.

It was, therefore, concluded that the methanol-soluble portion and methanol-insoluble residue consist of the condensed-type linkages of lignin due to a preferential degradation of the ether linkages of lignin occurred during supercritical water treatment.

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### References

- [1]Saka S. Ueno, T. *Cellulose*. 6, 1999, p. 177-191.
- [2]Saka S. Konishi, R. *Conference on Developments in Thermochemical Biomass Conversion*. Tyrol Austria. Sep 17-22, 2000, in press.